

Effect of Surfactants on the Solubility of Herbicides

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The effect of ionic and nonionic surfactants and urea on the solubilities of the herbicides pendimethalin [*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine] (Pend) and trifluralin [2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl)benzenamine] (TF) was studied. The solubility of both herbicides increases linearly with the concentration of the surfactant beyond their cmc and the slopes of the plots increase in the order SDS < CTAB < Tween 20 for TF and SDS < CTAB \approx Tween 20 for Pend. In all cases Pend is more soluble than TF at the same concentration of the additive. Urea solutions at concentrations higher than 2 M also increase the solubility of Pend more than that of TF. The solubility of both herbicides in mixtures of urea and surfactant is about or somewhat lower than that in a solution of the surfactants alone.

INTRODUCTION

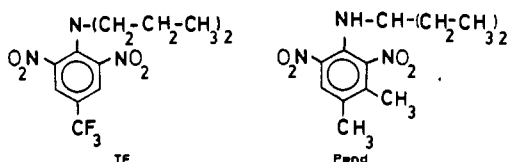
Molecules known as surface-active agents possess polar and nonpolar characteristics. They are able to remain in solution at higher concentrations by orienting themselves in aggregates known as micelles. Surfactants are widely used as a means of producing aqueous solutions of insoluble or poorly soluble drugs. This phenomenon is known as micellar solubilization, and it has been studied extensively in the past decades (Fendler, 1982).

Solubilization is the basis of many industrial processes and is of fundamental importance in rationalizing micellar effects on reactivity (Fendler and Fendler, 1975).

Nonionic surfactants are the most popular in pharmaceutical formulations. This is due mainly to their low toxicity, and numerous studies on the solubilities of various drugs in these surfactants have been reported (Ismail et al., 1970a,b). Furthermore, apple growers (Atwood et al., 1987) often combine fungicides, insecticides, foliar nutrients, and surfactants to reduce spraying time and cost.

Dinitroanilines with substituents on the aromatic ring and on the nitrogen are commonly used as herbicides. They are poorly soluble in water (1 ppm at 25 °C), and this limited solubility represents a problem in formulating aqueous preparations (Melnicov, 1971).

For this reason we considered it of interest to study the effect of additives such as surfactants and urea on the solubility of pendimethalin [*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine] and trifluralin [2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl)benzenamine], which are herbicides frequently used in our country, and the results are reported in this paper.



MATERIALS AND METHODS

Pendimethalin (Pend) was obtained from a commercial sample of Herbadox (Cyanamid) and purified by recrystallization from ethanol/water 1:1, mp 56–57 °C [lit. mp 56–57 °C (*The Merck Index*, 1983)] [see Worthing (1979) for toxicological information].

Trifluralin (TF) was obtained from a commercial sample of Treflan (Eli Lilly) and purified by recrystallization from etha-

nol, mp 46–47 °C [lit. mp 46–47 °C (*The Merck Index* 1983)] [see Worthing (1979) for toxicological information].

SDS (Mallinckrot) was recrystallized twice from EtOH/water (1:1) and vacuum dried (Duynstee and Grunwald, 1959).

CTAB (Sigma) was recrystallized from MeOH/acetone and then washed with anhydrous ether and vacuum dried (Evans et al., 1988).

Tween 20 (Sigma) was used without further purification.

Solubility determinations were made by shaking excess herbicide in various concentrations of aqueous surfactants, urea, and urea-surfactant solutions during 24 h in a constant water bath temperature at 25 °C. This time was found to be sufficient for attaining equilibrium. After equilibrium, aliquot portions of the supernatant liquid were removed, filtered, and centrifuged. The extinction coefficient at the wavelength of maximum absorption of both herbicides was determined and measured in aqueous surfactants and urea solutions at concentrations above the cmc. These values are 1931, 2020, and 2172 for TF and 1422, 1500, and 1604 for Pend in SDS, Tween 20, and CTAB, respectively.

Absorption was then used to calculate the concentration of both herbicides. The UV-vis spectra and absorbance measurements were obtained by using a Shimadzu UV-260 spectrophotometer.

RESULTS AND DISCUSSION

Solubilization in Aqueous Surfactant Solutions. The solubility of TF and Pend in the presence of surfactants with different head groups, SDS (anionic), CTAB (cationic), and Tween 20 (nonionic), was determined.

The observed changes in solubility below the cmc for the three surfactants are within the limits of experimental error, but it increases beyond this value and does not reach a maximum even up to 9×10^{-2} , 2×10^{-2} , and 0.2×10^{-2} M for SDS, CTAB, and Tween 20, respectively. The plots of solubility of TF and Pend are shown in Figures 1 and 2, where it can be seen that at a given surfactant concentration Pend is more soluble than TF. The break in the curves of Figures 1 and 2 occurs at the surfactant concentration coincident with the cmc, namely 8.1×10^{-3} M (SDS) and 0.92×10^{-3} M (CTAB), in good agreement with reported values (Fendler, 1982). The solubility of both herbicides increases linearly with the concentration of the surfactants beyond their cmc, and the slopes are collected in Table I. The observed linearity indicates that the solubilization increases but the amount of free solubilize (*S*) and the average number of molecules per micelle (\bar{S}) are constant over all the range studied. The slopes can be used to calculate the equilibrium constants for the

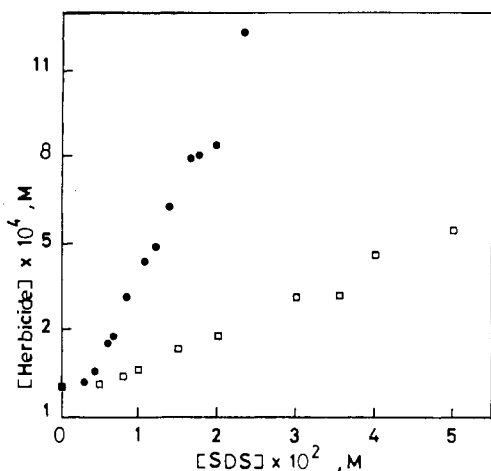


Figure 1. Effect of SDS on the solubility of Pend (●) and TF (□) in water at 25 °C. cmc = 8.1×10^{-3} M.

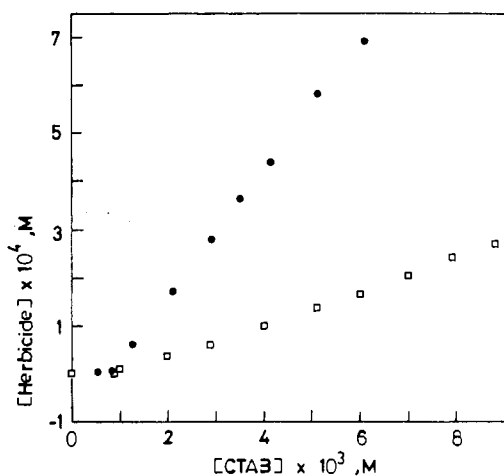


Figure 2. Effect of CTAB on solubility of Pend (●) and TF (□) in water at 25 °C. cmc = 0.92×10^{-3} M.

Table I. Maximum Solubilizing Power of Surfactants for Herbicides at 25 °C

herbicide	mol of herbicide/mol of surfactant		
	SDS	CTAB	Tween 20
TF	1.2×10^{-2a}	3.4×10^{-2b}	5.3×10^{-2}
Pend	6.3×10^{-2c}	13.0×10^{-2d}	12.0×10^{-2}

^a $K_1 = 3.7 \times 10^6 \text{ M}^{-1}$, calculated from eq 2 with $N = 65$ (Moroi, et al., 1982). ^b $K_1 = 10 \times 10^6 \text{ M}^{-1}$, calculated from eq 2 with $N = 60$ (Kalyanasundaram, 1987). ^c $6 \times 10^6 \text{ M}^{-1}$ (see footnote a). ^d $12 \times 10^6 \text{ M}^{-1}$ (see footnote b).

association between the solubilize and the micelle (M) (eq 1) provided that the aggregation number (N) of the



micelle is known (Moroi et al., 1982). Assuming that the distribution of the solubilizes among the micelles follows the Poisson distribution, eq 2 is derived, where S_t is the

$$S_t = SK_1[M] + S \quad (2)$$

molar concentration of the herbicide and $M = (M_t - \text{cmc})/N$. The values of K_1 calculated are indicated in Table I, but they are only approximate because TF and Pend are very insoluble in water and the absorbance measure is very small; however, the values are useful for comparison purposes.

The slopes of the solubility isotherms are a measure of the solubilizing capacity of the surfactants. From these values it is evident that Tween 20 is the best surfactant for TF while Tween 20 and CTAB are much better than SDS for Pend. The anionic SDS is less effective in dissolving both herbicides.

It is known (Klevens, 1950) that nonionic surfactants have a solubilizing power greater than ionic surfactants at the same concentration. They are frequently used in herbicidal and fungicidal activity determinations (Kirino et al., 1987, 1988), and this is due to their low toxicity combined with their good solvent action.

Solubilization was established to be a dynamic process involving both hydrophobic and electrostatic interactions. In micellar systems polar molecules are considered to associate with the surfactant head groups, while apolar ones are predominantly located in the micellar core (Fendler, 1982). According to this model, the solubilized herbicide should be in the micellar core.

There are numerous factors with regard to the structure of the solubilize that affect the amount of solubilization of the compounds. Among them, the polarity, charge, molar volume, chain length, branching, substitution, and planarity are found to be important in determining the degree to which compounds will dissolve in the detergent micelles (Klevens, 1950). The first systematic attempt to correlate these characteristics of the solubilize with the extent of solubilization was made by McBain and Richard (1946), who investigated a wide range of compounds. They concluded that the chemical nature of the solubilize is much more important than molecular weight. For example, methyl *tert*-butyl ether is more strongly solubilized by aqueous solution of dodecylamine hydrochloride at 25 °C than 2,2-dimethylbutane is, although they have almost the same molecular weight. The conclusions drawn by other authors show that molecular weight, molar volume, and chemical nature play an important role in solubilization (McBain and Hutchinson, 1955).

According to the calculation of $\log P$ using Rekker fragmental constants (Rekker, 1977), the hydrophobicity of TF is about the same as that of Pend; therefore, the different solubilities of both compounds cannot be attributed to this factor. Besides, the equilibrium constants K_1 are quite similar for both herbicides in each surfactant, so the increase in the slopes corresponding to Pend is mainly determined by the different solubilities of both compounds in water, namely 6×10^{-6} and $2 \times 10^{-6} \text{ M}^{-1}$ for Pend and TF, respectively. The higher solubility of Pend may be attributed to the fact that Pend has an NH group capable of forming a hydrogen bond with water.

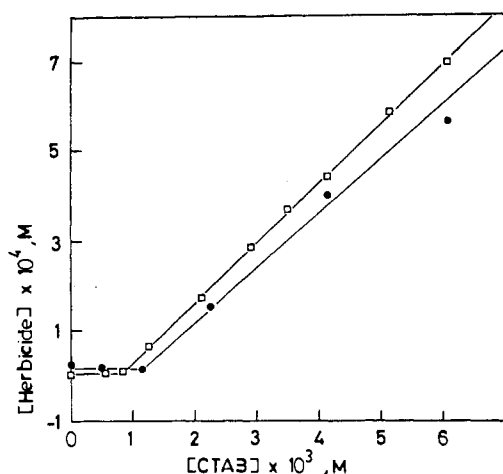
The different behaviors observed with micelles of different charge type reveal that the hydrophobic core of the micelle is necessary for solubilizing water-insoluble or weakly soluble compounds but dipolar molecules or molecules with polarizable electrons interact very differently with micelles of opposite charge (Armstrong and Stine, 1983).

Solubilization in Aqueous Urea Solutions. Urea, an achiral planar molecule which itself is soluble to the extent of 16.65 M in water (*The Merck Index*, 1989), is well-known for its ability to improve the water solubility of a variety of nonpolar as well as polar organic molecules (Pharr et al., 1989), and it is also used as a soil nutrient (Primo Yufera and Carrasco Dorien, 1973).

We have carried out solubility determinations in aqueous urea solutions. At urea concentrations below 2 M, none of the herbicide solubilities were modified. For concen-

Table II. Effect of Urea on the Solubility of Pendimethalin and Trifluralin at 25 °C

[urea], M	[trifluralin] × 10 ⁶ , M	[pendimethalin] × 10 ⁶ , M
2.01		1.13
4.00	0.5	2.60
6.00	0.7	5.00
8.01	0.9	10.90
10.11		12.20

**Figure 3.** Effect of CTAB on the solubility of Pend in water (□) and in 4 M urea (●) at 25 °C.

trations higher than 2 M, the solubility increased for both herbicides (see Table II). Again, Pend is more soluble than TF.

The solubilities of both herbicides in urea-surfactant mixtures were determined, and the solubilizing capacity of these mixtures was compared with those of aqueous urea and surfactant solutions. The solubility of Pend and TF in solutions containing SDS in the 0.5–2 × 10⁻² M range and 2 or 4 M urea is the same as that observed in solutions without urea. Solutions containing 6 M urea and 0.3–2 × 10⁻² M SDS become cloudy during assay so the solubility could not be determined under these conditions. Similar results were obtained with CTAB and 6 M urea. On the other hand, the solubility of Pend and TF could be determined in the presence of CTAB and 4 M urea. As Figure 3 shows, the cmc of CTAB increases under these conditions and the solubility is somewhat lower than in the absence of urea.

It is known (Emerson and Holtzer, 1967) that increasing the concentration and hydrophobic character of an additive changes the cmc of the surfactant systems. In general, the organic additives are not as effective in breaking up SDS micelles as they are in breaking up DTAB micelles. Urea at 25 °C presents a striking case of this: 2 M urea raises the cmc of DTAB by 46%, and 6 M urea raises it by 306%; the corresponding values for SDS are 16 and 104% (Emerson and Holtzer, 1963). Our results indicate that 4 M urea increases the cmc of CTAB by 34%.

The increase in the solubility of TF and Pend in the presence of urea may indicate a decrease in unfavorable interactions between the nonpolar group of the herbicides and the solvent as water molecules are replaced by urea in the solvation shell. The fact that the solubility of Pend increases more than that of TF indicates that there are specific interactions between the herbicides and urea. Molecular recognition in aqueous solution is a well-known phenomenon (Endo et al., 1989).

Spectral Shifts of Solubilized Species. The spectra of two herbicides in polar and nonpolar solvents were compared with the spectra in surfactant solutions to have

qualitative evidence of the microenvironments. The spectrum of TF and Pend in dioxane is shifted 10 nm toward lower wavelengths than the spectrum in DMSO. The same shift is observed when TF and Pend are solubilized in CTAB, SDS, and Tween 20, indicating that the solubilize is in a less polar environment.

A similar blue shift is observed when both herbicides are solubilized in aqueous urea solutions.

CONCLUSIONS

The solubility of each herbicide in aqueous solutions containing surfactant was found to be linearly dependent on the surfactant concentrations beyond their cmc.

In aqueous urea solutions the herbicide concentrations increased at urea higher than 2 M.

The effect of additives is stronger in the solubility of Pend than that on TF.

The spectral shifts indicate that the herbicides are in a less polar environment when they are solubilized in urea and surfactant solutions.

These results may be of interest for the formulation of the herbicides.

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Registry No. SDS, 151-21-3; CTAB, 57-09-0; Tween 20, 9005-64-5; pendimethalio, 40487-42-1; trifluralin, 1582-09-8; urea, 57-13-6.